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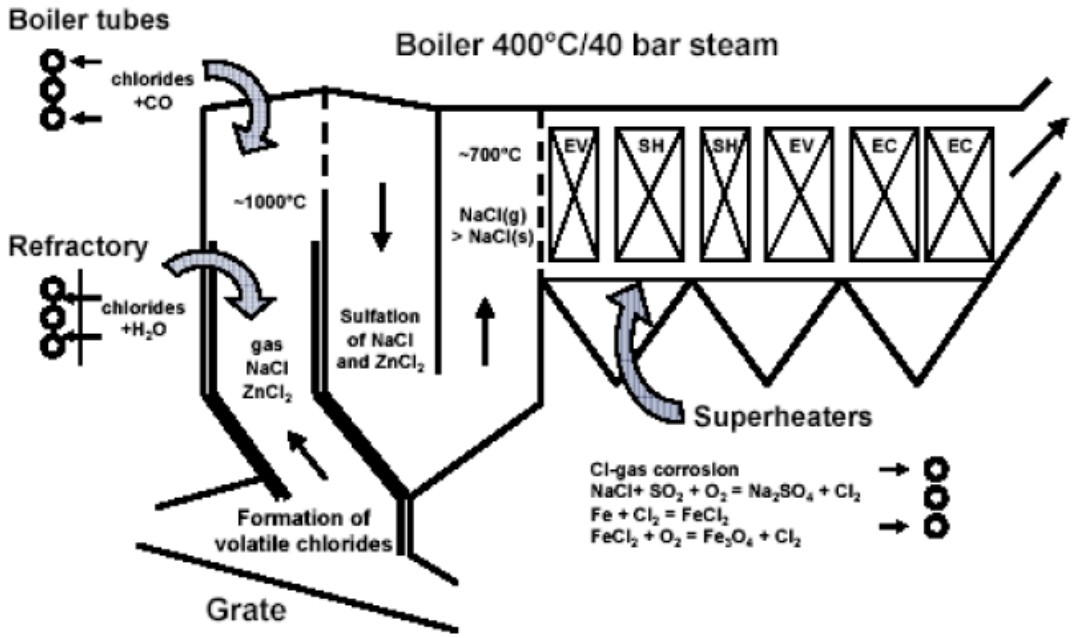

Next Generation of High-Efficient Waste Incinerators

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Abstract

Modern society produces increasing amounts of combustible waste which may be utilized for heat and power production, at a lower emission of CO_2, e.g. by substituting a certain fraction of energy from fossil fuel-fired power stations. In 2007, 20.4 % of the district heating and 4.5 % of the power produced in Denmark came from thermal conversion of waste, and waste is a very important part of a future sustainable, and independent, Danish energy supply [Frandsen et al., 2009; Grøn Energi, 2010].

In Denmark, ~ 3.3 Mtons of waste was produced in 2005, an amount predicted to increase to 4.4 Mtons by the year 2030. According to Affald Danmark, 25 % of the current WtE plant capacity in Denmark is older than 20 years, which is usually considered as the technical and economical lifetime of WtE plants. Thus, there is a need for installation of a significant fraction of new waste incineration capacity, preferentially with an increased electrical efficiency, within the next few years.

Compared to fossil fuels, waste is difficult to handle in terms of pre-treatment, combustion, and generation of reusable solid residues. In particular, the content of inorganic species (S, Cl, K, Na, etc.) is problematic, due to enhanced deposition and corrosion – especially at higher temperatures. This puts severe constraints on the electrical efficiency of grate-fired units utilizing waste, which seldom exceeds 26-27%, campared to 46-48 % for coal combustion in suspension.

The key parameters when targeting higher electrical efficiency are the pressure and temperature in the steam cycle, which are limited by high-temperature corrosion, boiler- and combustion-technology. This report reviews some of the means that can be applied in order to increase the electrical efficiency in plants firing waste on a grate.

Introduction

A number of factors, acting singly or in concert, have been identified as potential causes of corrosion in Waste-to-Energy (WtE) plants. These factors include feedstock composition, design features and operating conditions such as temperature, velocity, and gas/solid composition. The combination of these factors inside the WtE boiler is complex, and a detailed understanding of the release, ash formation and flue gas chemistry, has not yet been achieved. The environment in WtE plants is dynamic and constantly changing, with local regions alternating between oxidixing and reducing environments, even though the unit operates at an overall excess of O_2. Deposits forming on heat transfer surfaces also promote reducing conditions at the deposit/scale interface. Poor combustion characteristics of the waste may cause regions of incomplete combustion, including localized reducing conditions (high CO-levels), high heat flux from flame impingement, and possibly the presence of chemically aggressive species in deposits. Low-melting metal chlorides deposited on heat transfer surfaces break down the protective oxide scale, thereby allowing dissolution of alloy elements

like Fe and Cr into the molten inner deposit layer, and, thereby, subsequently rapid oxidation [Wright and Krause, 1996].

The influence of different corrosion factors can be summarized as follows [Lee et al., 2007]:

- ***Metal surface temperature***: High temperature of metal surfaces due to high radiation fluxes accelerates the melting of deposits and increases the corrosion rate. In general, the metal temperatures of waterwall and superheater tubes are maintained at temperatures of about 300 ^{o}C and 450 ^{o}C, respectively.
- ***Gas temperature***: The temperature of the combustion gases can affect both deposition rates and deposit compositions and therefore accelerate the corrosion rate. The temperature gradient between gas temperature and metal surface temperature is a driving force for the condensation of gaseous species, e.g. metal chlorides, on the cooled surface. At a large temperature gradient, the chloride concentration in the deposit is high and the initial deformation temperature of the deposit decreases. Also, thermal stresses induced by the temperature gradient across the deposit can affect the adhesion and structure of oxide scales on metal tubes (causing cracks in the protective oxide scale and increase diffusion within oxide scales, thereby affecting the oxidation kinetics).
- ***Temperature fluctuation***: The non-homogeneous composition of waste fuels and the uneven temperature profile in the flue gas channel cause sharp fluctuations in the gas temperature. Experimental studies have confirmed that the corrosion rate increased several times because of temperature fluctuation.
- ***Characteristics of molten salt deposits***: The diffusion rate of corrosive gases through cracks and pores of deposits is an essential factor for increasing corrosion. The presence of HCl, SO2, and alkaline and heavy metal components in deposits can affect both chemical and physical properties of deposits such as gas permeability of deposits.

Corrosive interactions between deposits and heat transfer surfaces puts severe constraints on the electrical efficiency of the grate-fired units, which seldom exceeds 26-27%. In general there are two major corrosion mechanisms in WTE facilities [Lee et al., 2007]:

- ***Active oxidation***: This mechanism occurs at metal temperatures above 450 ^{o}C and comprises several steps: (a) the formation of chlorine at the scale surface; (b) penetration of chlorine into the scale to the oxide/metal interface; (c) formation of chlorides on the metal surface components; (d) diffusion of metal chloride vapors outwards; (e) reaction of the metal chloride with available oxygen in the atmosphere to give metal oxide and chlorine.
- ***Corrosion due to deposits by sulfation and by molten salts***: Gases containing Cl_2, HCl, and gaseous alkali chlorides, e.g. NaCl and KCl, can accelerate the active oxidation. Also, volatilized salt chlorides carried in the sulfide gases are deposited on the boiler tubes during cooling and contribute to corrosion in two ways: (1) the chlorinated species in the deposit cause a reaction similar to gas phase/active oxidation; (2) the presence of chlorides in the deposits may result in the formation of low-temperature melting eutectics (salt solution characterized by the lowest

possible melting point) which may flux (dissolve) the oxide layer that is protecting the metal surface.

Accumulated operating experience has led to reduced corrosion in the boiler tubes. Over the years, the industry has adopted general approaches to reduce corrosion which can be classified as primary and secondary measures. Primary measures seek to eliminate corrosion by influencing the process conditions in the boiler. Some of the methods include [Albina, 2005]:

- Improvement of process control, in particular minimizing fluctuations in gas temperature, and;
- Design modifications, such as process gas recirculation to alter flow dynamics, enhancing gas mixing through the use of process gas recirculation, and design of the boiler system (e.g. horizontal vs. vertical boiler).

Secondary methods of protection are applied to extend the lifespan of the boiler tubes. In the past ten years, many kinds of corrosion-resistant material systems have been tested and applied to actual boilers. For example, high Cr - high Mo nickel-base alloys and high Cr-high Si ferronickel alloy tubing products are now being used in WTE plants. Furthermore, coating systems such as High Velocity Oxygen Fuel (HVOF) thermal spray and weld overlay have been developed and applied to advanced WTE boilers. Other classical secondary measures include the injection of chemicals to remove deposits and use of refractory lining and ceramic tiles in the lower half or the entire height of the combustion chamber.

Below are further details of some protection methods that have been applied in WTE facilities or are still under investigation, [Albina, 2005];

- **Adoption of Inconel Alloy 625 cladding and composite tubes:** Application of a ceramic cladding is connected with a number of technical and economical problems, such as large overall dimensions of a power unit or the necessity to use a recirculation system for cooling the boiler. Such systems may turn out to be very costly, technically complicated, and expensive to use. For this reason, since the 1980s, departure has been observed from ceramic cladding in favour of composite tubes and pad welding [Adamiec, 2009]. Waterwall and superheater tubes are the most corrosion sensitive areas. This technique consists of overlaying a layer of Alloy 625 (21Cr-9Mo-3.5Nb-Ni base) on these tubes to protect them from the attack of HCl/Cl_2. This method has been used successfully on the waterwall tubes and part of the superheater tube bundles in many WTE facilities. The key element regarding the cost is how much Alloy 625 should be used and where. Although the price of Alloy 625 is higher than that of a protective refractory lining, the cost of Alloy 625 can be partly compensated by avoiding the cost of refractory maintenance. The application of Alloy 625 on the superheater tubes is more complicated since its performance on superheater tubes depends on the metal temperature. One study showed that Alloy 625 does not provide protection above 400 – 420 ^{o}C. Another indicated that at metal temperature of about 540 ^{o}C, the wastage rate of Alloy 625 is 0.2µm/h. Some boilers of existing WTE facilities are designed to operate at lower temperatures and therefore can apply Alloy 625 on superheater tube bundles. However, problems still arise in these WTE facilities because the lifetime of Alloy 625 cladding is unpredictable. It may last as much as two years, or as little as

three months. For new WTE facilities, where boilers are designed to operate at higher temperatures, the Alloy 625 cladding on superheater tube bundles is not recommended.

- **Different designs of flue gas pass of boilers:** In general, there are two major flow-pass designs of boilers: vertical and horizontal. Regarding erosion-corrosion, the basic idea is to minimize impact velocity, create a uniform flow pattern, and smooth transition from the 1st to the 2nd pass. Under the same operating conditions, superheater tube bundles in a vertical design, which has fewer gas passes will have more critical corrosion problems than that in a horizontal design since the former are subjected to higher metal temperatures and flow velocities of flue gas [Albina, 2005]. The Seghers Prism, which is a prism-shaped tube equipped with several tuyeres through which secondary air is injected into the combustion gases as they rise above the combustion grate. It is inserted horizontally through the center of the combustion chamber at the lower end of the first radiant boiler pass. It is water-cooled and refractory lined. Corrosion phenomena can be reduced since the function of the prism is to mix the combustion gases, increase turbulence and decrease temperature fluctuation, thus minimizing hot spots.
- **Recirculation of flue gas:** In some of the most recent WtEs part of the flue gas is recirculated through secondary tuyeres in the combustion chamber. This has similar beneficial effects (better mixing, increased turbulence, fewer hot spots) as those claimed for the Seghere Boiler Prism.
- **Injection of chemicals into combustion chambers:** The objectives of injection of chemicals such as Ca(OH)2 or Mg(OH)2 into combustion chambers are to (a) decrease HCl concentration in the flue gas; (b) facilitate the removal of deposits and decrease their corrosion potential. This method is still under investigation, but the preliminary result has shown to be effective. The disadvantage is that continuing injection of chemicals is required and this increases the cost of operation and also the amount of fly ash.
- **Improvement of cleaning method:** Some on-line methods for cleaning heat exchanger tubes, such as high pressure water washing and explosive cleaning have been developed in order to limit the build-up of deposits. These cleaning methods are effective in removing the slag and ash deposits; however they also cause the erosion-corrosion on some area of the superheater tubes. Furthermore, some cleaning methods require WtE plants to come off-line for complete cleaning. Therefore, improvement of cleaning methods which can be less harmful to the tube life without reducing the cleaning efficiency is needed [Albina, 2005].

Two types of additives may be applied to affect the alkali-S-Cl chemistry in the freeboard or minimize deposit formation in WtE plants; the first type fixes the alkali metals chemically, thereby releasing Cl to the gas phase, most likely as HCl(g), while the second type of additive consists of ash particles designed to get trapped inside deposits in the actual plant. Due to their chemistry these additive particles will then inhibit the sintering/consolidation of the deposit and make it easier to remove the deposit by e.g. soot-blowing or mechanical cleaning. Anyhow, recent research on the release of alkali and heavy metals, S and Cl from various types of biofuels and well-characterized waste fractions, has revealed a significant potential of in-bed removal of flame-volatile elements like K, Na, Zn, Pb, and S.

Affecting the Release of Me, Cl and S from the Fuel Bed

Quantification of the release of inorganic elements, Cl and S, and heavy metals to the gas phase during combustion of waste fractions was until recently almost unknown. Besides the risk of harmful emissions to the environment inorganic elements released from the grate may cause severe ash deposition and corrosion problems in the boiler, subsequently leading to decreased overall efficiency and costly, unscheduled shut-downs. Therefore, a study was conducted in order to obtain quantitative data on the release of inorganic elements from well-characterized waste fractions; in order to understand the release pattern and the link to formation of fly ash and aerosols in full-scale waste incinerators [Pedersen et al., 2009].

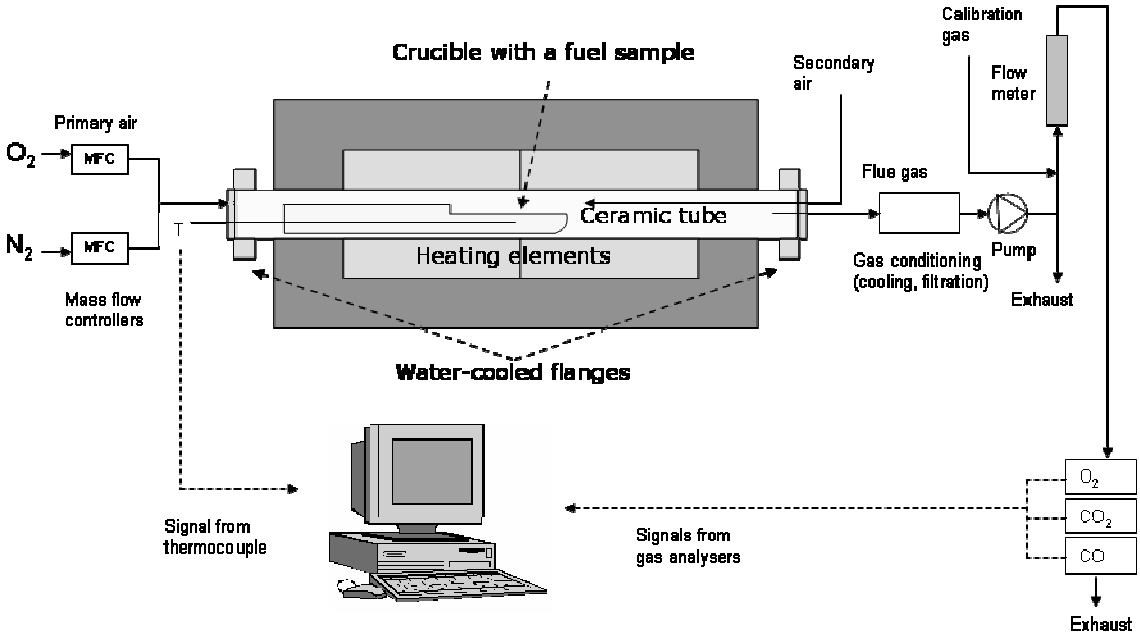


Figure 1: Sketch of experimental set-up for release quantification [Pedersen et al., 2009].

A lab-scale setup at DTU Chemical Engineering, Technical University of Denmark (DTU) was applied for the experimental release study. The setup including a gas mixing system, an electrically heated, horizontal tube reactor, a gas conditioning system, gas analyzers, a thermocouple and a data acquisition system, allowed for pyrolysis and combustion under well-controlled conditions. A sketch of the set-up is shown in Figure 1.

Batch experiments with sample sizes of 2 – 10 g were conducted at different temperatures in the interval [500 – 1150 ^{o}C]. The release of inorganic metals (Na, K, Pb, Zn, Cu), S and Cl from annual energy crops, wood fuels as well as four dedicated waste fractions has been quantified. The biomass and waste fuels were characterized by use of wet chemical analysis, and, based on the chemical composition of the initial fuel sample and the ash residue after the experiments; the release of inorganic elements was quantified [van Lith et al., 2006, 2008; Pedersen et al., 2009].

For the waste fuels investigated, in terms of total release potential, PVC, shredder waste and shoes were identified as the most risky waste fractions. PVC showed a very high (relative and total) release potential for Pb (~3.5 g/kg), and, in particular, for Cl (~480 g/kg). In the case of shredder waste, high initial concentrations of heavy metals and alkalis gave rise to a high total release potential (release of [Na+K+Zn+Pb+S] > 33 g/kg) for this waste fraction. A relatively high total release potential was also found for shoes (release of [S+Cl+Zn] ~ 40 g/kg), whereas for CCA impregnated wood the release of highly toxic As was identified as the main concern when burning this waste fraction [Pedersen et al., 2009].

The influence of fuel composition was also studied by comparing the release trends obtained for four different wood fuels (spruce, beech, bark, and fiber board) [van Lith et al., 2006, 2008];

A high release of Cl was observed during combustion of bark and fiber board (~85% and ~99% release, respectively) at a temperature as low as 500 °C. The Cl contents of spruce and beech were too low to even quantify the Cl-release during combustion, but a (nearly) complete release at 500 °C is expected also for these fuels. The principal mechanism for the release of Cl from wood fuels is believed to be the reaction of metal chlorides with carboxyl groups or other proton-donating sites in the char during pyrolysis, resulting in the formation of HCl(g). The organic structure of the fuel (the availability of proton-donating sites) therefore plays an important role in controlling the Cl release during wood combustion at 500 °C [van Lith et al., 2006, 2008].

Sulfur was released in two steps in the case of all four wood fuels. Organically associated S was released below 850 °C, whereby the main fraction is released below 500 °C. The fraction of S released below 850 °C is therefore strongly dependent on the ratio of organic- versus inorganic S in the fuel, rather than on the inorganic composition of the fuel. In the temperature range of 850–1150 °C, the inorganic S is gradually released, probably mainly because of the incorporation of alkali and alkaline earth sulfates in silicate structures, whereby SO_2(g) is released [van Lith et al., 2006, 2008].

The release of K and Na was found to be strongly dependent on both the temperature and the fuel composition under the investigated conditions. Potassium and Na are released by similar mechanisms. Because of the low Cl contents of the fuels, and since most of the Cl was released at 500 °C, the fraction of K and Na released by vaporization of KCl and NaCl was found to be limited. More likely, the release up to ~800–850 °C is due to the release of some of the char-bound alkali metals (originating from organically associated alkali metals and/or from alkali chlorides that have reacted with the char during pyrolysis), and depends on the organic structure of the fuel and its decomposition behavior during pyrolysis. Above ~850 °C, the release of K and Na was strongly dependent on the inorganic composition of the fuel, and is probably mainly a result of the decomposition of alkali carbonates. Most likely, the Si-content of the fuel affects the K-release during wood combustion above 800 °C [van Lith et al., 2006, 2008].

The release of the heavy metals Zn and Pb started around 500 °C and increased sharply to more than 85% at 850 °C in the cases of spruce, beech, and bark, and is therefore mainly dependent on the temperature. The release mechanisms are believed to be the reduction of Zn and Pb compounds to the volatile compounds Zn(g) and PbO(g) during the pyrolysis stage. Some retention of Zn and Pb occurring in the range of 850–1150 °C may be due to the partial incorporation of Zn and Pb into (alumino-) silicates. Of the four investigated wood fuels, fiber board showed the lowest fractions of S, K, Na, Zn, and Pb released, most likely because of the presence of Ti in the coating [van Lith et al., 2006, 2008].

Thus, the release studies conducted by [van Lith et al., 2006, 2008; Novakovic et al., 2009; Pedersen et al., 2010] provided strong preliminary indications that it is possible to affect the total release of metals, S and Cl by secondary interactions with char and/or ash inclusions in the fuel-bed, which may again cause decreased deposition and corrosion and thereby increased electrical efficiency in these plants. A complete review of release studies conducted previously is presented by [Frandsen and Pedersen, 2010b].

Interactions are possible between elements being released in the bottom of the fuel-bed and char particles or ash inclusions (especially ash inclusions rich in Si, Ca and P) present higher up in the fuel-bed. This may cause secondary capture of already released elements.

[Novakovic et al., 2009] conducted a fundamental study in order to quantify the release of K from simple synthetic salt systems, and to obtain information on the effects of the elements Ca, Si, and P on retaining K in residual ash. Furthermore the effects of temperature, the presence of water vapor, the speciation of K and Ca, and the sample size, on the release rate of K from the simple ternary systems K-Ca-Si and K-Ca-P were investigated. Well-defined mixtures of K, Ca, and Si (or P) species were heat-treated in a reactor, at constant temperature (900 or 1000 °C), in a gas flow of 4 Nl/min N_2 containing 2% (v/v) H_2O. Average release rates were calculated from weight measurements of the samples after every 15 min of the heat treatment (and subsequent cooling to room temperature) [Novakovic et al., 2009].

The presence of water in the gas flow was found to significantly enhance the K-release rate, from both the K-Ca-Si, system and the K-Ca-P system. For the K-Ca-Si system, a significantly higher release rate was observed at 1000 °C, compared to 900 °C. Furthermore, doubling the Ca/Si molar ratio in the K_2CO_3-CaO-SiO_2 mixture strongly enhanced the K-release rate (by about 2 times) at 1000 °C [Novakovic et al., 2009]. This suggests that SiO_2 preferentially reacts with CaO, so that more K is being released to the gas phase instead of being incorporated into the silicate structure. For the K-Ca-P system, with K_2CO_3 as the K source, the Ca/P molar ratio had a strong effect on the K-release rate: a decrease in the Ca/P molar ratio (or increase in the P content) significantly decreased the K-release rate from the K-Ca-P mixtures. As opposed to the K-Ca-Si system, it thus seems that K is preferentially incorporated in (non-volatile) $(K_2O)_k{\cdot}(CaO){\cdot}(P_2O_5)_m$ structures. The effects of temperature and Ca source on the K-release rate from this system were limited but most pronounced for the mixtures with the highest Ca/P ratio (lowest P content) [Novakovic et al., 2009].

In addition, the sample size had a strong influence on the K-release rate. In the case of K-Ca-P mixtures containing KCl as the K source, the K-release rate was significantly higher at 1000 °C compared to 900 °C in the first 15 min of the heat treatment, whereas the Ca/P ratio had no effect on the K-release rate [Novakovic et al., 2009].

For both the K-Ca-Si and K-Ca-P systems, with K_2CO_3 as the K source, the presence of water in the gas flow significantly enhances the K-release rate. This is most likely due to the enhanced rate of decomposition of K_2CO_3 in the presence of water vapor, forming KOH(g) [Novakovic et al., 2009].

For the K-Ca-Si system, the K-release rate is significantly higher at 1000 °C than at 900 °C. Furthermore, doubling the Ca/Si molar ratio of a K_2CO_3-CaO-SiO_2 mixture strongly enhances the K-release rate (by about 2 times), at 1000 °C. This suggests that SiO2 preferentially reacts with CaO, so that more K is being released to the gas phase, instead of being incorporated in the silicate structure. The use of $Ca(OH)_2$ as the Ca source instead of CaO does not influence the release rate from the K_2CO_3-Ca source-SiO_2 mixture at 1000 °C [Novakovic et al., 2009].

For the K-Ca-P system with K_2CO_3 as the K source, the Ca/P molar ratio has a strong effect on the K-release rate: a decrease in Ca/P molar ratio (or increase in the P content) significantly decreases the K release. As opposed to the K-Ca-Si system, it thus seems that K is preferentially incorporated in (nonvolatile) $(K_2O)_k \cdot (CaO)_l \cdot (P_2O_5)_m$ structures. The effects of the temperature and Ca source on the K-release rate in this system are limited but most pronounced for the mixtures with the highest Ca/P ratio (lowest P content), which is the composition resembling residual ash from wood chips. Doubling the sample size (i.e., sample layer thickness) results in a lower but not half as low K-release rate, probably because of transport limitations [Novakovic et al., 2009].

In the case of K-Ca-P mixtures, containing KCl as the K source, the Ca/P ratio has no effect on the K-release rate. The K-release rate is significantly higher at 1000 °C compared to 900 °C in the first 15 min of heat treatment. SEM-EDX and STA studies of selected samples confirmed the effects of the Ca/Si and Ca/P ratios and the speciation of K and Ca on the release behavior observed in the heating experiments [Novakovic et al., 2009].

There is a strong link between primary release of K, Na, Zn, Pb, S and Cl, secondary capture of these elements via chemical interactions with char particles or ash inclusions in the fuel-bed, and subsequent formation of fly ash and aerosols. This link and the serious gaps in the current understanding of these interactions have been thoroughly addressed by [Frandsen and Pedersen, 2010a], in a short summary version of a major review paper presented by [Frandsen et al., 2010].

The paper by [Frandsen et al., 2010b] are divided into three main sections, dealing with release of critical elements like K, Na, S, Cl, Zn and Pb, formation of aerosols and residual ash. There are a lot of high-quality data available on the release of critical elements, although most of the lab-scale measurements are performed under conditions different from what really happens in full-

scale. The main difference being the particle size distribution of the fuels investigated and the time-temperature history, mainly the heat-up rate. Anyhow, the data are available, and several good attempts have been made to derive mechanisms for the release of especially K, S and Cl, taking into account chemical interactions with other elements like Al, Si, Ca and P. Anyhow, there is still a big gap to fill out before we have a reasonable modeling of the release, from single particles and beds of burning fuels. Thus, we are still by no means able to provide reliable boundary conditions for e.g. advanced flow models to simulate freeboard chemistry etc. in these systems [Frandsen et al., 2010b].

At lot of focus has been but on aerosol formation when utilizing solid fuels, in the entire range of fuel qualities from coal, via wood fuels to annual biomasses and waste fractions. The fundamental aspects of aerosol formation from these fuels have been outlined via a significant number of measuring campaign, reported in the literature. We even have a good qualitative image of the mechanisms of aerosol formation for most of the fuels, and in some cases reliable 1st generation models for aerosols formation have been suggested, especially for coal-firing in suspension and straw-firing on a grate. Aspects of aerosol transport are also addressed thoroughly in the literature. Anyhow, there is also here a big gap to step over before these models are fully implemented in e.g. models for freeboard chemistry or advanced flow in furnaces [Frandsen et al., 2010b].

The last leg in the above outline, the residual ash formation, is well described for coal-firing in suspension, where even reliable models for prediction of chemistry and particle size distribution have been published and tested in the literature, while for utilization of many of the other fuels, the physical description of how the residual ash is formed is almost non-existing. The physical development of residual ash link to its fate further down the line in the actual combustion system; will it be lifted from the fuel-bed ?; will it be transported to the heat transfer surfaces, and in case yes, where will that happen ?; will it stick to the heat transfer surface upon impact ?; and, how will it transform and/or interact with e.g. gaseous species during transport up through the freeboard etc. ? Often, we have lots of chemical analyses of residual ash particles that have been collected in various positions when utilizing some of these fuels, but there is an almost complete lack of physical understanding and investigations in this area. How do these particles develop physically during the thermal fuel conversion process and what mechanisms are controlling this ? This will affect their size distribution and chemical composition [Frandsen et al., 2010b].

Thus, there a several gaps in our understanding of release and formation of aerosols and residual ash, although a lot of high-quality work has been conducted in these fields during the last 2-3 decades.

The main parameters controlling residual fly ash formation in thermal fuel conversion systems, are;

- The actual combustion temperature
- The residence time
- Stoichiometry (pyrolysis/combustion/gasification)

- Design of the combustion system (burner (suspension firing), grate (fixed bed combustion))
- Fuel particle size
- Fuel type (coal, biomass, waste fraction, blends)
- Ash content and inorganic composition
- Association of inorganic elements (organic vs. inorganic)

The influence of all of these parameters must be addressed in order to gain fundamental data on and understanding of how residual fly ash is formed. A preliminary study on residual ash formation from wood fuels were conducted at DTU Chemical Engineering, illustrating that careful design of experimental work may indeed provide very valuable how the chemistry and size distribution of fly ash develops, see [Frandsen et al., 2010a].

Slag-Tap Furnace

Another option, instead of fixing the flame-volatile elements like, K, Na, Zn and Pb by secondary chemical interactions within the fuel-bed and thereby decreasing the deposition and subsequent corrosion of heat transfer surfaces, is the slag-tap furnace concept that has proved successful for straw-firing in CHP-boilers based on grate-technology.

Several investigations of ash and deposit formation have been conducted at Danish straw-fired CHP-boilers, including Haslev, Slagelse, Rudkøbing, Masnedø and Maribo-Sakskøbing. Due to the very high concentrations of K and Cl released from straw, and the potential of corrosive attacks on heat transfer equipment, the metal temperature in the 1st generation straw-fired CHP-plants had to be kept rather low ~ 450 °C, in order to avoid too fast corrosion. Therefore, the 1st generation plants had relatively low electrical efficiencies. Anyhow, for the 2nd generation straw-fired CHP-plants, the final superheater temperature has been increased to ~ [520 – 540 °C], causing a higher electrical efficiency [Frandsen, 2009].

Thus, a certain modification of the boiler design may help minimize the corrosive problems, e.g. by changing the contact pattern between the hot flue gas and the heat transfer sections which may affect the corrosion in the actual boiler. The Masnedø and Maribo-Sakskøbing CHP-boilers are examples of boilers designed to collect a rather thick depost/slag layer on the superheater tubes, instead of trying to avoid deposit formation. Investigations at both plants revealed that the inner layer in this boiler was extensively sulfated after a certain operation time, and that the K_2SO_4-rich inner layer actually helped to protect the heat transfer surfaces from further corrosive attack [Frandsen, 2009].

Fly ash from straw-firing on a grate is rich in K, Si and Ca, which will form molten silicate in deposits formed along the pendent superheaters. This is part of the receipt behind the success of the slag-tap furnace since a high liquid fraction on the superheater deposits will cause accelerated deposit formation. Anyhow, fly ash formed during waste-firing on a grate, has a completely different chemistry, dominated partly by sulfates (of K, Na and Ca). Such ashes have no 3-D structure like the K-Ca Silicates formed in straw-fired systems, they are composed by cations and anions distributed in such a way that they ensure an overall electrical neutral

mixture. When molten, sulfates run like water. Further, sulfates and silicates (which are also present in ashes formed in WtE plants) may not be fully miscible, meaning that there is a risk of forming a two-phase system, which may not support the slag tap superheater concept. Thus, a limiting factor for the use of slag-tap furnaces in waste-fired systems may be the melting, viscosity and rheology of these ashes.

[Arvelakis and Frandsen, 2005; Arvelakis et al., 2007, 2008a,b] conducted a preliminary study in order to investigate the melting behaviour of fly ashes from incineration of municipal solid waste. Four fly ash samples from the Svendborg WtE (waste-to-energy) plant (2^{nd}–3^{rd} pass, superheater, economizer, ESP), in Denmark, were investigated by use of a high-temperature rotational viscometer in order to determine their rheology, and by a hot-stage XRD in order to identify phase changes in these ashes during cooling.

The ash samples tested melt at temperatures below 1300 °C, and maintain their Newtonian flow characteristics, even at temperatures approaching 1100 °C in some cases. Leaching of the alkali salts from the ash samples leads to melting at higher temperatures [Vargas, 2001]. Measurements performed under similar conditions reproduced well especially in the Newtonian flow range. Use of high rotational speeds at temperature segments where crystallization occurs dissolves the crystals/solids in the melt and lowered the point of critical viscosity T_{CV} of the melt, while use of low rotational speeds gave the opposite effect [Arvelakis and Frandsen, 2005; Arvelakis et al., 2007, 2008a,b].

Hot-stage XRD data have shown that the ash solidify mainly as non-crystalline materials. At temperatures below 1000 °C, most of the ashes re-crystallized but the crystalline compounds observed were different compared to those during the heating stage. Hot-stage XRD data and viscosity measurements were found to correlate well [Arvelakis and Frandsen, 2005; Arvelakis et al., 2007, 2008a,b].

The conclusions from the preliminary study of waste ash rheology were that, much more work is needed in order to verify the potential success of a slag-tap furnace for waste-firing on a grate.

The Steam Boost® Process

[Jensen et al., 2010] proposed two different concepts that could potentially increase the plant's electrical efficiency. The first possible concept is shown in Figure 2 and is termed the 'flue gas split concept'. In essence, part of the flue gas from the grate combustion zone that is hot, but contains low amounts of corrosive ash species, is directed towards an extra high temperature superheater. A wall is inserted into the boiler chamber, which then leads part of the grate flue gas to a superheater that subsequently boosts steam temperature.

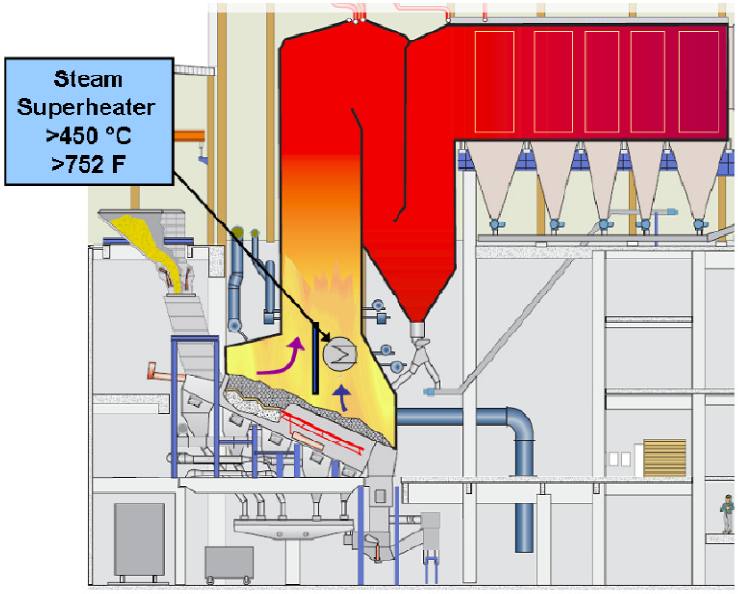


Figure 2: Possible set up of the flue gas split concept.

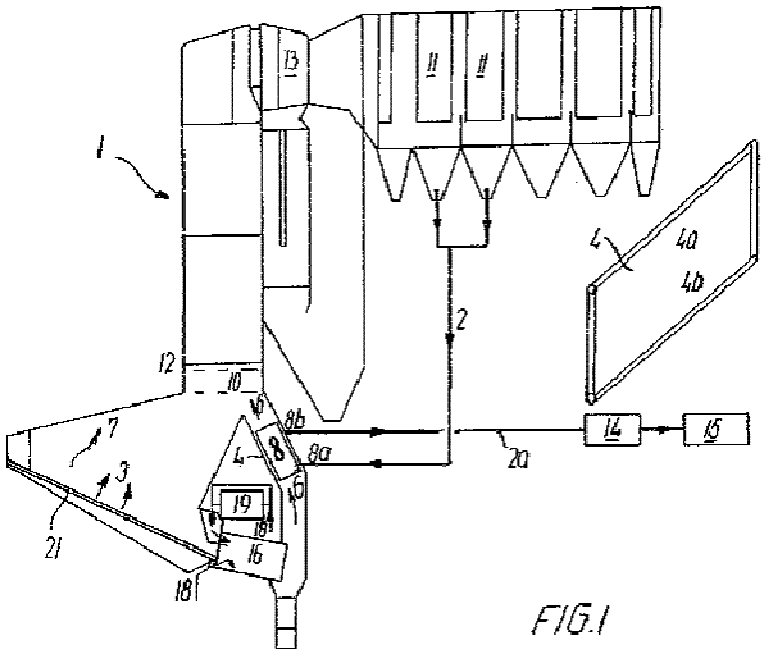


Figure 3: Concept of inserting a rotary kiln into a waste incineration plant, ensuring improved slag quality and provides a flue gas that can be used for extra steam superheating. Number explanations: 16: rotary kiln; 8: extra superheater; 19: gas burner.

The second patented concept is shown in Figure 3. The objective of this concept is to use a rotary kiln that could be heated by a gas burner to improve slag quality. At the same time, the hot flue gas leaving the rotary kiln may be used to superheat the steam to a high temperature, and thereby increase the plant's electrical efficiency. For several reasons the thermal rotary kiln treatment is seen as a promising technique in improving the leaching quality of bottom ashes. Thermal treatment can be carried out directly at the waste incineration plant, thereby reducing the costs compared to a stand-alone treatment facility. Rotary kiln ash treatment combines high temperature conditions, long retention time and good material mixing. The high temperature treatment induces changes in the bottom ash matrix, which generally result in both physical and chemical fixation of some metals and therefore lower heavy metal leaching. The combustion of residual organic matter, and the consequent lower leaching of soluble organic carbon (DOC), may cause a decrease in the leaching of elements that are mobilized by organic complexation (e.g. Cu and Pb) [Jensen et al., 2010].

[Jensen et al., 2010] reported the following scientific results:

- The influence of rotary kiln thermal treatment on the leaching of Ca, Al, Si, Mg, Ba, Sr, Cl, Cu, Pb, Zn, Cr, Mo, sulfate, DOC and carbonate has been determined.
- Combustion conditions above the grate of a waste incineration plant with respect to temperature, hydrocarbon release and concentration of O_2, CO_2 and CO have been determined.
- The release and concentration of volatile ash species as Cl, Na, K, Ca, Pb, Zn and S above the grate in a waste combustion plant have been determined.

The main technical results obtained in the project were [Jensen et al., 2010]:

- A flexible bench-scale gas-heated rotary kiln experimental facility was constructed, and experiments with bottom ash treatment and flue gas fly ash deposit formation were conducted.
- The rotary kiln thermal treatment of bottom ashes can be recommended to reduce the leaching of Cu, Pb, Cl, Zn and DOC; however, an increased leaching of Cr and Mo should be expected.
- Deposit probe measuring data indicate that the flue gas from a rotary kiln slag treatment process is not well suited for increasing superheater steam temperature in a waste combustion plant.
- For the volatile elements Cl, S, Na and K measured along the grate of a waste boiler at Vestforbrænding, the maximum concentrations were measured a few metres after the fuel inlet, while the concentrations decreased strongly further downstream of the grate. The conducted measurements show that flue gas from grate sections 3 and 4 can produce a sufficiently hot flue gas that only contains low concentrations of corrosive species. It will, however, require a steady control of the position of the grate fire.

- CFD calculations indicate the flue gas-dividing wall in the flue gas split concept needs some degree of refractory lining to prevent flue gas cooling too much.
- Implementation of the patented flue gas split concept on a waste combustion plant, and using a reasonable increase in final steam temperature from 400 to 500°C, has the potential to increase electrical efficiency from 24 to 30% (with respect to lower fuel heating value).

Based on the design, development and run-in of the rotary kiln reactor at DTU Chemical Engineering, the following recommendations regarding future work are provided [Jensen et al., 2010]:

- The use of additives in the form of clay minerals in a kiln treatment process may significantly improve both the properties of the flue gas (less corrosive) and the leaching properties of the treated ash.
- The leaching determinations conducted were carried out on pulverized material. The kiln treatment caused some melting and sintering that reduced leaching, so in future studies leaching determinations should also be performed on non-pulverized samples.
- To lead the way for the flue gas split concept, probe deposit measurements in the near grate zone should be conducted in a full-scale plant. The next step should be to insert an extra pilot superheater in a full-size waste combustion plant.
- Further rotary kiln treatment studies are needed to determine how all the changes in operating conditions influence changed ash leaching properties.

Corrosion and Material Aspects

When steel is exposed to an oxidizing environment at high temperature, the metal will gradually oxidize to thermodynamically stable oxides forming an oxide scale adjacent to the metal. This oxide scale acts as a barrier for further diffusion of oxygen to the metal. However, Cl_2 may have the capability to penetrate the scale by diffusion, and react with Fe, forming $FeCl_2$, which is stable at low O_2-concentrations. $FeCl_2$ has a high vapour pressure and may diffuse outward through the scale, where it oxidizes to solid Fe_2O_3 as the partial pressure of O2 increases. The Fe_2O_3 formed by this process is however much more porous, and the chlorine gas released by the process is able to diffuse back and further attack the metal. This corrosion process, whereby chlorine plays a catalytic role, is referred to in the literature as 'active oxidation'.

The presence of SO_2 (or SO_3) in the flue gas may cause sulphation of the alkali chlorides in the deposits, e.g., in the case of KCl:

$$2\,KCl(s) + SO_2(g) + O_2(g) \rightarrow K_2SO_4(s) + Cl_2(g) \qquad (1)$$

$$2\ KCl(s) + SO_2(g) + ½\ O_2(g) + H_2O(g) \rightarrow K_2SO_4(s) + 2\ HCl(g) \qquad (2)$$

As a result of this sulphation reaction, the Cl_2/HCl released from the inner deposit-layer close to the heat transfer surface may increase the corrosion rate by the 'active oxidation' process.

[Andersson et al., 2004] studied the corrosion of two austenitic alloys inside solid KCl, focusing on the effect of deposit morphology in late stage corrosion. Metal coupons were embedded in tablets of KCl that were pressed and shaped to mimic certain features of boiler deposits. The features that was examined are the deposit porosity and thickness as well as the occurrence of cracks and edges.

The observations showed clearly that the deposit morphology does affect the corrosive attack [Andersson et al., 2004]. The reactions that occurred were formation of oxides and chromates:

$$4\ KCl + Cr_2O_3 + 5/2\ O_2 \rightarrow 2\ K_2CrO_4 + 2\ Cl_2$$

$$4\ KCl + Cr_2O_3 + 2\ H_2O + 3/2\ O_2 \rightarrow 2\ K_2CrO_4 + 4\ HCl$$

Both reactions include consumption and formation of gaseous species. Further reactions may also lead to formation of volatile metal chlorides. The transport of all these gaseous species through the deposits will certainly affect the reaction rates. It was noted that chlorine was frequently observed at the metal oxide interface. When data from all morphologies was gathered it was clear that the deposit thickness had a strong influence on the reaction products [Andersson et al., 2004].

The effect of the deposit thickness shows a strong correlation to observations in an earlier field test, where the fastest attack for both alloys occurred along the edge of the deposit. Alloy 310 was more sensitive to the deposit thickness than Sanicro 28. Further, high-density samples were generally less corroded than low-density but the attacks were less even, and more severe towards the rim of the tablets. Due to the lower deposit permeability, the high-density samples are likely to be more sensitive to defects in the deposits induced during sample preparation and handling [Andersson et al., 2004].

Waste fractions (with exception of PVC) has generally low contents of K, S and Cl, but compared to other solid fuels such as annual biomass fuels, chemically untreated wood chips, or coal, the concentrations of heavy metals such as Zn and Pb are much higher in several of the waste fractions fired. The presence of these in deposits, especially as chlorides plays an important role, as they form low melting eutectics, which may cause severe corrosion, due to the dissolution of the oxide scale in the melt.

In order to gain insight into corrosion in waste-fired furnaces, corrosion tests were performed in the corrosion test-rig at DTU Chemical Engineering, in which boat-like test elements of 15M03 (a common ferritic steel applied in waste-fired boilers, see Table 1), were covered with synthetic deposits, and exposed isothermally at 500 °C, to a synthetic gas mixture (see Table 2).

Table 1: Composition of 15Mo3 (values in wt%)

C	Si	Mn	Mo	Fe
0.17	0.20	0.60	0.30	Balance

Table 2: Synthetic Flue Gas Composition, Simulating Waste Wood Firing

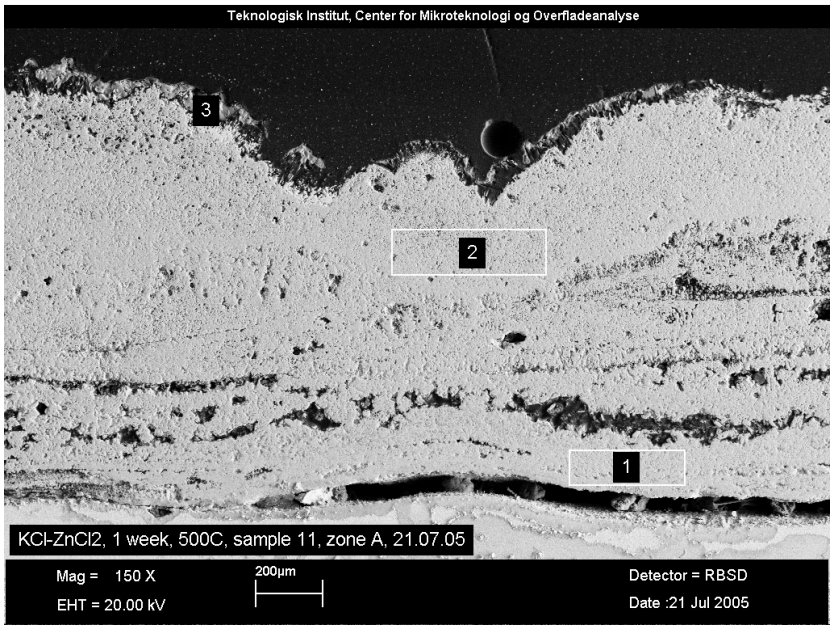
O_2	CO_2	SO_2	HCl	N_2	H_2O
8 % (v/v) (dry)	14 % (v/v) (dry)	140 ppmv (dry)	75 ppmv (dry)	balance	2-3 % (v/v)

A worst case scenario was chosen for the deposit compositions, namely binary and ternary mixtures of KCl, ZnCl2 and PbCl2. With regard to K, Zn, and Pb, the mixtures were blended in molar ratios corresponding to common concentrations found in full-scale deposits, see Table 3. According to phase diagrams, all of the investigated mixtures are present as melts at 500 °C, except the $ZnCl_2$–$PbCl_2$ mixture. Samples without deposit were exposed to the same conditions, as a reference.

Table 3: Deposit Compositions Used in the Corrosion Tests

System	Molar ratios		
	K	Zn	Pb
KCl-$ZnCl_2$	0.5	0.5	
KCl-$PbCl_2$	0.95		0.05
$ZnCl_2$-$PbCl_2$		0.95	0.05
KCl-$ZnCl_2$-$PbCl_2$	0.49	0.48	0.03

After 1, 2, and 4 weeks of exposure, the corroded specimens were withdrawn from the reactor, and studied in detail in a scanning electron microscope (SEM). The chemistry of the corrosion layers was identified by SEM-EDX, and the thickness of the oxide scale was determined by multiple measurements in the SEM. This was done for each exposure time, and for each deposit composition, in order to determine the influence of deposit composition, on the corrosion rate.



Zone A	Si	S	Cl	K	Mn	Fe	Zn
1	0.9	0.4	4.2	1.1	0.3	92.1	1.1
2	0.2	0.7	0.4	0.9	0.3	95.7	1.9
3	0.3	12.3	1.8	17.7	0.4	2.4	65.2

Figure 4: Sample covered with a KCl–$ZnCl_2$ deposit, exposed for 1 week. The sound metal is situated in the bottom of the picture. Compositions in mol%, C- and O-free.

SEM analyses on the reference samples (metal specimens without deposit) revealed a very thin oxide scale of 16 ± 6 µm, after 1 and 2 weeks exposure, consisting of pure iron oxide. After 4 weeks exposure, the thickness of the oxide scale had increased to 64 ± 20 µm.

For the metal specimens coved with a deposit, the compositions of the oxide scales reflect the active corrosion mechanism. For example, SEM-EDX analysis of the oxide scale formed after 1 week exposure of a metal specimen covered with a KCl–$ZnCl_2$ deposit, indicated the presence of Cl (most likely as $FeCl_2$) near the metal/scale surface, and S together with traces of Zn, K, and Cl in the outer layers of the oxide scale (see Figure 4). The EDX analysis at point 3 in this image indicates that this is the remainder of the synthetic deposit. A high concentration of S compared to Cl is measured, indicating that that the original KCl–$ZnCl_2$ deposit has sulphated to a significant degree, through reaction with SO_2 from the synthetic flue gas applied. Furthermore, the SEM pictures reveal rather porous oxide scales, which is in agreement with the suggested corrosion mechanism.

After 4 weeks exposure of the test element covered by KCl–$ZnCl_2$ deposit, a distinct band of $FeCl_2$ was present just above the test element, as can be seen in Figure 5, and even more clearly in the X-ray mappings presented in Figure 6. The X-ray mappings also show that K, S, and Zn are present at similar locations within the corrosion products, indicating a sulphate melt of K, Zn, and iron oxide.

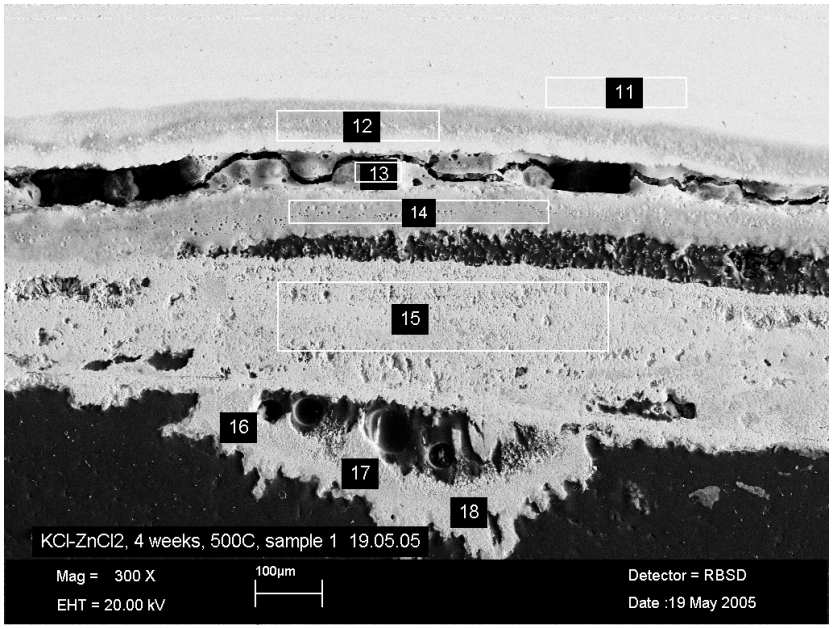


Figure 5: SEM-EDX analysis of a sample covered with a KCl–$ZnCl_2$ deposit, exposed for 4 weeks. The sound metal is situated in the top of the picture. Compositions in mol%, C- and O-free. The bar indicates 100 µm.

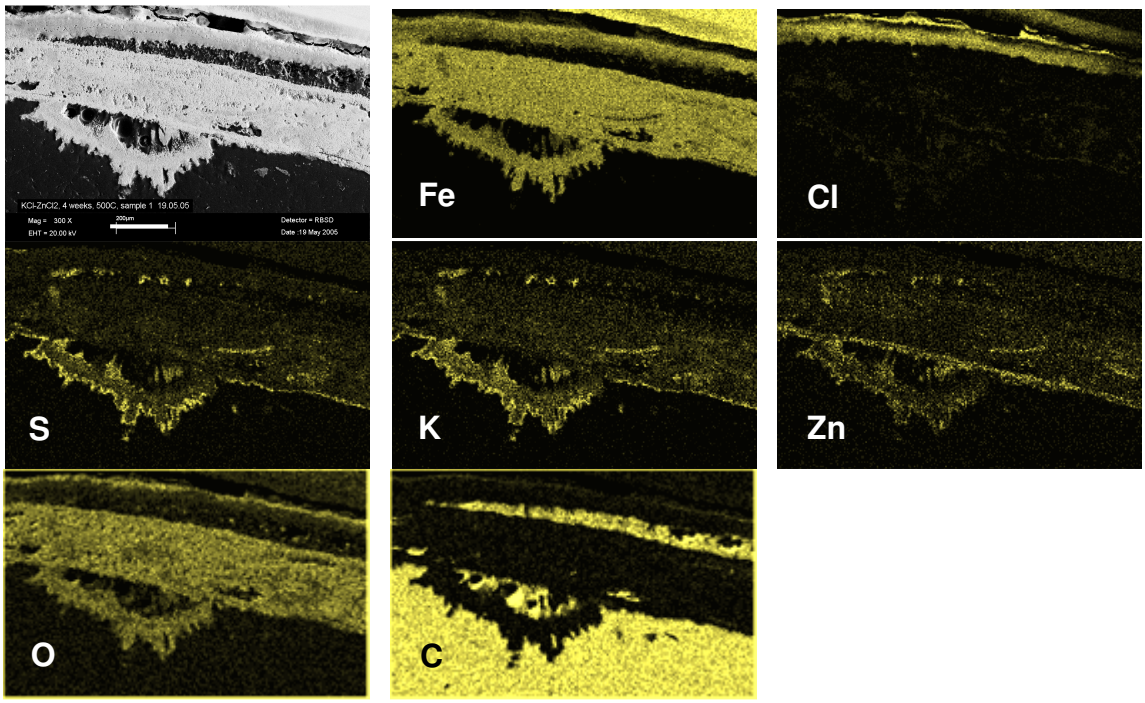


Figure 6: X-ray mappings of different elements the area similar to Figure 8-2. The first picture is the backscattered image. The bar indicates 200 µm.

The thickness of the oxide scale after 1, 2, and 4 weeks exposure was measured in the SEM at 7 to 20 locations, within each sample. An overview of the results is presented in Figure 7. The

figure clearly shows that the corrosion rate is strongly enhanced in the presence of chlorides. However, after 2 and 4 weeks exposure, the thickness of the oxide scale is not very uniform for most of the samples (possibly due to non-uniform distribution of the mixtures onto the test elements, or due to inhomogeneous mixtures), which makes it difficult to see a trend in the corrosion rate. For the test elements coved with the deposit systems KCl–$ZnCl_2$, KCl–$PbCl_2$, and KCl–$ZnCl_2$–$PbCl_2$, it seems that the thickness of the oxide scale increases from 1 week to 2 weeks exposure, but then remains the same towards 4 weeks exposure.

The corrosion behaviour of the specimens covered with the $ZnCl_2$–$PbCl_2$ deposit remains unclear. The thickness of the oxide scale after 1 week exposure is similar to that in the presence of the KCl–$ZnCl_2$ and KCl–$PbCl_2$ deposits, but it then decreased and appears to be more similar to that of the reference deposit after 2 and 4 weeks exposure. The lack of accelerated corrosion in the presence of a pure $ZnCl_2$ deposit exposed at 500 °C was also observed by [Spiegel and Grabke, 1991]. According to their findings, this is due to the inward diffusion of Zn into the oxide scale and the formation of a Zn- and Fe-rich spinel, which is insoluble in the $ZnCl_2$ melt.

Thus, to sum up, the oxide scale thickness on a metal test element covered by a synthetic deposit (mixtures of KCl, ZnCl2 and PbCl2), and exposed to waste-firing conditions was found to be considerably larger than that of a reference test element exposed to the same conditions. This indicates that the corrosion attack is strongly enhanced by the presence of metal chlorides in the deposit, i.e., by deposit-induced chlorine corrosion.

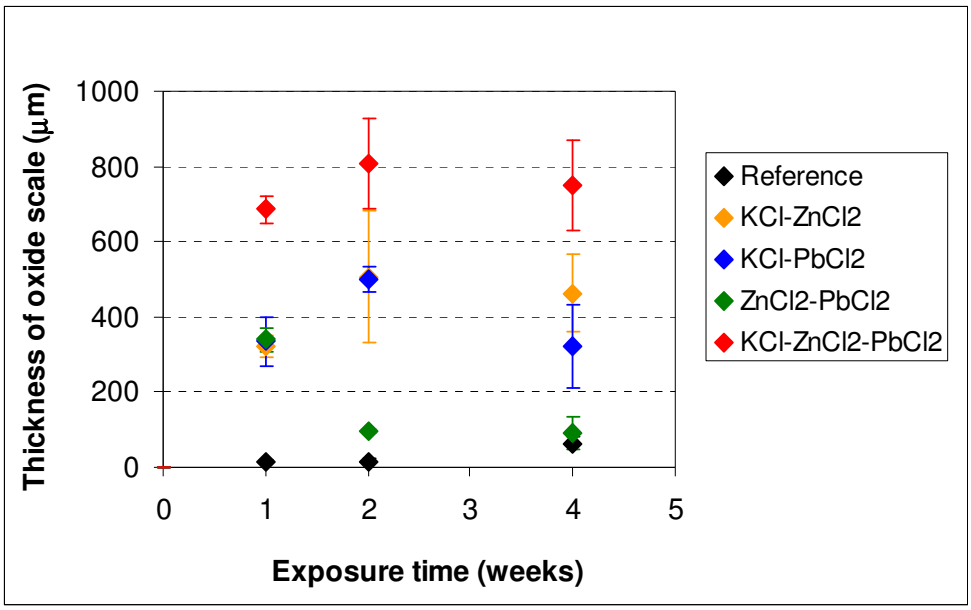


Figure 7: Thickness of oxide scale (µm) for reference samples and specimens covered with the difference deposit systems.

The preliminary lab-scale corrosion study conducted at DTU Chemical Engineering showed in accordance with [Andersson et al., 2004] that the amount of deposit (and thus the amount of

Cl in the deposit) present on the test elements, had a strong influence on the corrosion rate. When applying the same amount of deposit onto each test element, variations in the measured corrosion rate (oxide scale thickness) were minimised for most of the investigated deposit systems.

The observed corrosion rates for the Cl-based systems investigated were very high (ranging from ~150 μm to ~1 mm/month), but should be considered as the worst case scenario, as the synthetic deposits consisted of mixtures of chlorides of K and/or Zn and/or Pb. In a superheater deposit formed in a waste wood fired boiler, other ash-forming elements (e.g., S, Na, Ca, Mg, and Si) are present, which will influence the concentration of Cl in the deposit and the melting behaviour of the deposit, as was outlined in details in FORSKEL-5820 [Frandsen and van Lith, 2009].

The results indicated that corrosive potential of deposits consisting of mixtures of chlorides of K and/or Zn and/or Pb decreases in the following order: $KCl–ZnCl_2–PbCl_2$ > $KCl–ZnCl_2$ > $KCl–PbCl_2$ > $ZnCl_2–PbCl_2$. A homogeneous deposit composition and a uniform distribution of the deposit on each test element are necessary in order to obtain accurate corrosion rate laws.

Based largely on the experimental work presented by [Frandsen and van Lith, 2009] some ideas and suggestions to further work has been gained:

1. The effects of deposit composition (e.g., using Al_2O_3 or CaO instead of SiO_2 as was used mainly in FORSKEL-5820) on the sulfation and corrosion behavior, needs further attention. Tests with fly ashes from waste-fired boilers instead of the synthetic deposits should be carefully done.
2. The effect of shift in the temperature – both the gas temperature in the reactor, which is here assumed to be the same as the metal temperature, but also differences between gas and metal temperatures, and/or dynamic changes in the gas composition – e.g. changes in $[SO_2]$ or [HCl] vs. time - as experienced in real plants needs further attention, via systematic measurements.
3. The effect of different materials and coatings does also need further investigation. Several relevant superheater materials and coatings are available.
4. It may also be worth studying the contact between the synthetic deposits and the test elements further, i.e. addressing the effect of deposit porosity. In FORSKEL-5820 we applied powdery deposits, but deposits formed by evaporation of water from an aqueous solution of the relevant salts or a salt melt may provide a tighter contact, and thereby probably a changed corrosion pattern.
5. Further attention on other cat-ions, like Zn^{2+}, and, Pb^{+} and Pb^{2+} is definitely needed in order to extrapolate the results obtained here to eg. waste incinerators.

Acknowledgement
The work was carried out at the Combustion and Harmful Emission Control (CHEC) Research Centre, DTU Chemical Engineering, Technical University of Denmark (DTU). The CHEC Research Centre is co-funded by Dong Energy, Vattenfall AB, the Danish Energy Research Program, Energinet.dk, NordEn Research, the Technical Research Council, and the European Union.

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